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KINETIC REACTION COEFFICIENTS IN ROCKET EXHAUST PLUMES. (U)

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AFOSR-TR-77-1220

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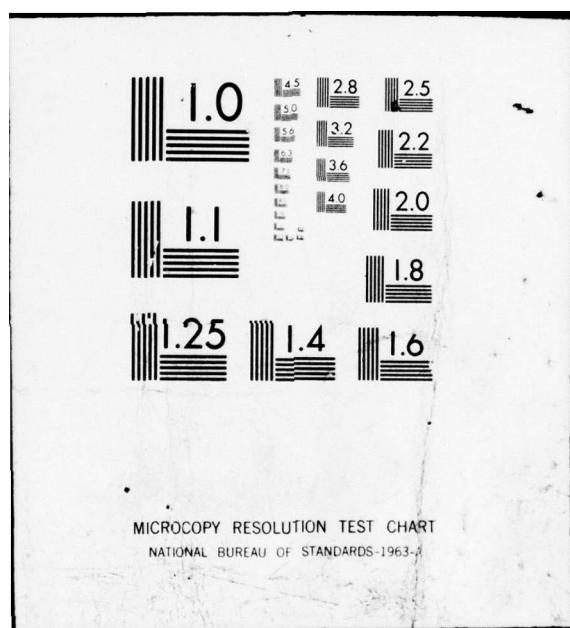
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KINETIC REACTION COEFFICIENTS
IN ROCKET EXHAUST PLUMES

1 July 1976 - 30 June 1977

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ABSTRACT

A review and analysis of available experiments and theory indicate that the rate constant for associative detachment of H and Cl⁻ is $1 \times 10^{-9} \text{ cm}^3/\text{sec}$ and is independent of temperature below 3600°K. The inverse reaction has a threshold energy of 0.64 eV and a preexponential constant of 5×10^{-10} gives a reasonable fit to available measurements. At low temperatures clustering of HCl and Cl⁻ ions is a rapid process. Drift tube measurements yield a value of $k = 10^{-25} \text{ cm}^6/\text{sec}$ at E/N = 12 Td. Progress on a crossed beam measurement of collisional ionization of potassium by atomic chlorine is discussed. A pulsed dye laser has been used to form a K⁺-e plasma in an argon buffer at 680 Torr by a two photon process. Analysis of the 6²S-4²P transition in the recombination spectrum yields a preliminary value for the three body recombination rate constant of $6.3 \times 10^{-28} \text{ cm}^6/\text{sec}$. at 473°K.



1. INTRODUCTION

Pergament and Jensen¹ recently have developed a model for estimating the densities of neutral and charged species for an afterburning plume of a solid fuel rocket as a function of distance along the plume. They have compared the predicted electron densities with experimental radar cross section measurements of electron density and find agreement at least within an order of magnitude. The predictions of the model are dependent on the accuracy with which the rate constants used are known. This report describes our progress in measuring rate constants for those reactions that Pergament and Jenson pointed out as critical to the model and poorly known; dissociative detachment of H + Cl⁻, collisional ionization of potassium and chlorine, and three body recombination of potassium.

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2. DISSOCIATIVE ATTACHMENT IN HCl.

Work has been completed on the reaction $e + HCl \rightleftharpoons H + Cl^-$ during this period. In the forward direction this reaction would be a source of Cl^- and a possible rapid energy loss mechanism for fast electrons. The reverse reaction is relatively fast at plume temperatures and is probably the dominant reaction which produces free electrons from Cl^- ions formed by collisional ionization with potassium.

For non-equilibrium calculations of particle densities in the plume, the individual forward and backward rates must be known. Christophorou² has made measurements of the forward rate which gave anomalously high results at plume temperatures. We have found that this difficulty is likely due to an impurity in the gas. Mass analysis of the ions formed at low E/N shows that they are highly clustered, and we have measured the rate for the formation of the first cluster. Christophorou also measured the cross section for dissociative attachment in a crossed beam experiment so that the threshold energy for the process is known. A measurement of the reverse reaction has been made by Herzenberg³ at 300°K in a flowing afterglow. This low temperature measurement can be extrapolated to several thousand degrees with the results of a theoretical treatment of associative detachment by Herzenberg. The sum of these measurements yields an estimate of the reaction rates which should improve the modeling of the plume electron density profile.

Christophorou's beam experiment gives a threshold for $e + HCl \rightarrow H + Cl^-$ of 0.64 eV so that the exponential term in the general rate form, $k = Ae^{-\Delta E/kT}$, becomes $-7440/T$. Figure 1 is a plot of Christophorou's swarm measurement of attachment in HCl in which his measurements of α_w versus E/P has been transformed k versus T. The rate in cm^3/sec is related to α_w by $3.5 \times 10^{16} k = \alpha_w$. The E/P scale is transformed by means of a table of measured electron mean energy as a function of E/P in nitrogen given by Christophorou⁴ where $T \sim \frac{\langle E \rangle}{k}$. A fit of

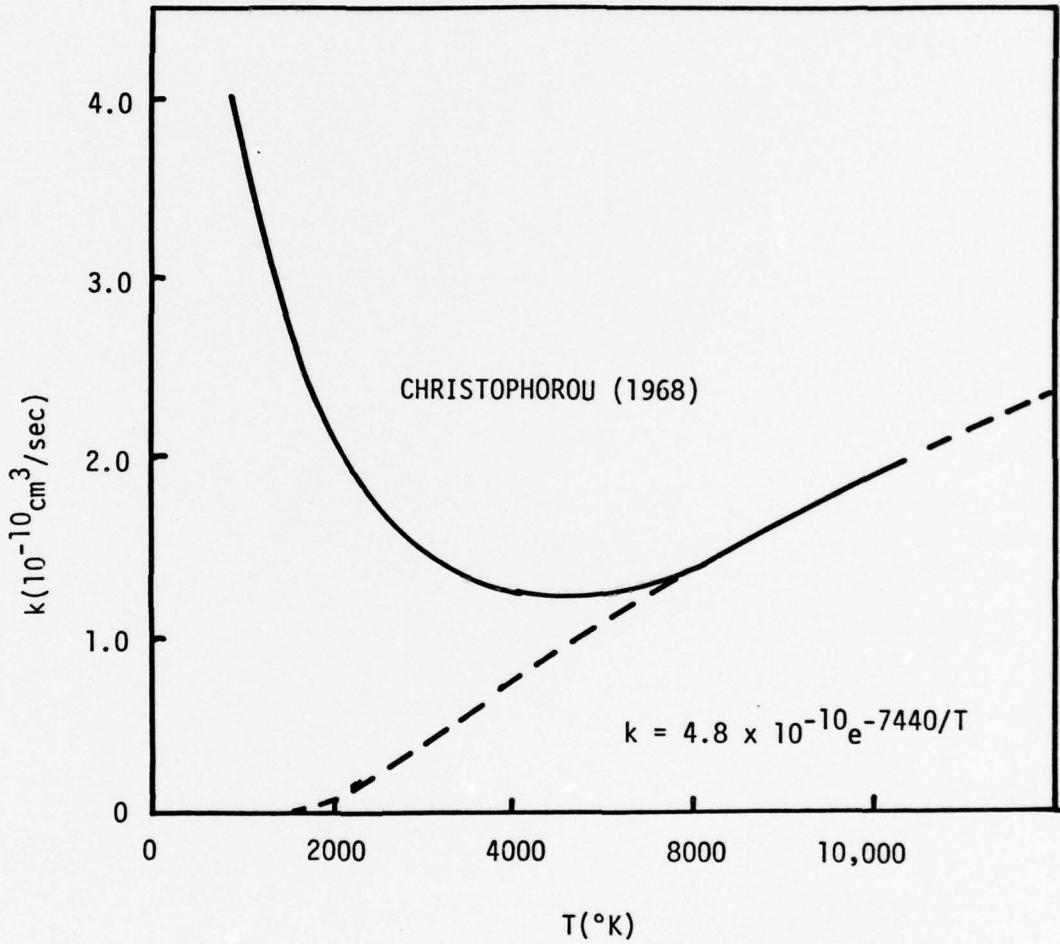


FIGURE 1. Dissociative Attachment in HCl. Solid curve is adapted from swarm measurement by Christophorou². Dashed curve is a plot of $k = 4.8 \times 10^{-10} e^{-7440/T}$.

$k = Ae^{-7440/T}$ to the high temperature end of the curve in Fig. 1 should determine the preexponential constant A. The rapid rise at low temperatures is not due to $e + HCl \rightarrow H + Cl^-$ and is most likely due to dissociative attachment to an impurity, such as CCl_4 or Cl_2 , which has a relatively sharp peak in the cross section near zero electron energy. The dashed curve is a plot of $k = Ae^{-\Delta E/kT}$ for $A = 5 \times 10^{-10}$ and $\Delta E = 0.64$ eV. The dash-dotted curve is for $A = 1 \times 10^{-10}$ and $\Delta E = .86$ eV which Pergament and Jensen used in their model calculations.

At plume temperatures of the order of 1600^0K the exponential term will depress the rate two orders of magnitude so that $k_f \approx 5 \times 10^{-12} \text{ cm}^3/\text{sec}$. However, the rate of the reverse reaction is about $10^{-9} \text{ cm}^3/\text{sec}$ so that the equilibrium concentrations will strongly favor $e + HCl$ over $H + Cl^-$.

Herzenberg⁵ has shown that for temperatures below a few thousand degrees the cross section for associative detachment, for collision partners that will form a molecule in which the dissociation energy is larger than the electron affinity of the ion, is essentially equal to the Langevin spiraling cross section when the kinetic energy of the collision is small.

Essentially all of the collisions result in $A^- + B \rightarrow AB + e$, if $EA(A) + KE < D(AB)$. The Langeviu cross section depends on the polarization potential and leads to an expression for the cross section of

$$\sigma \approx \frac{(2\pi)^2 \alpha e^2}{E}^{1/2}$$

Since the reaction rate is approximately given by:

$$\bar{k} \approx \bar{\sigma} \bar{v} = \sigma \sqrt{2E/u},$$

the rate is

$$\bar{k} \approx \left(\frac{4\pi^2 \alpha p^2}{\mu} \right)^{\frac{1}{2}}$$

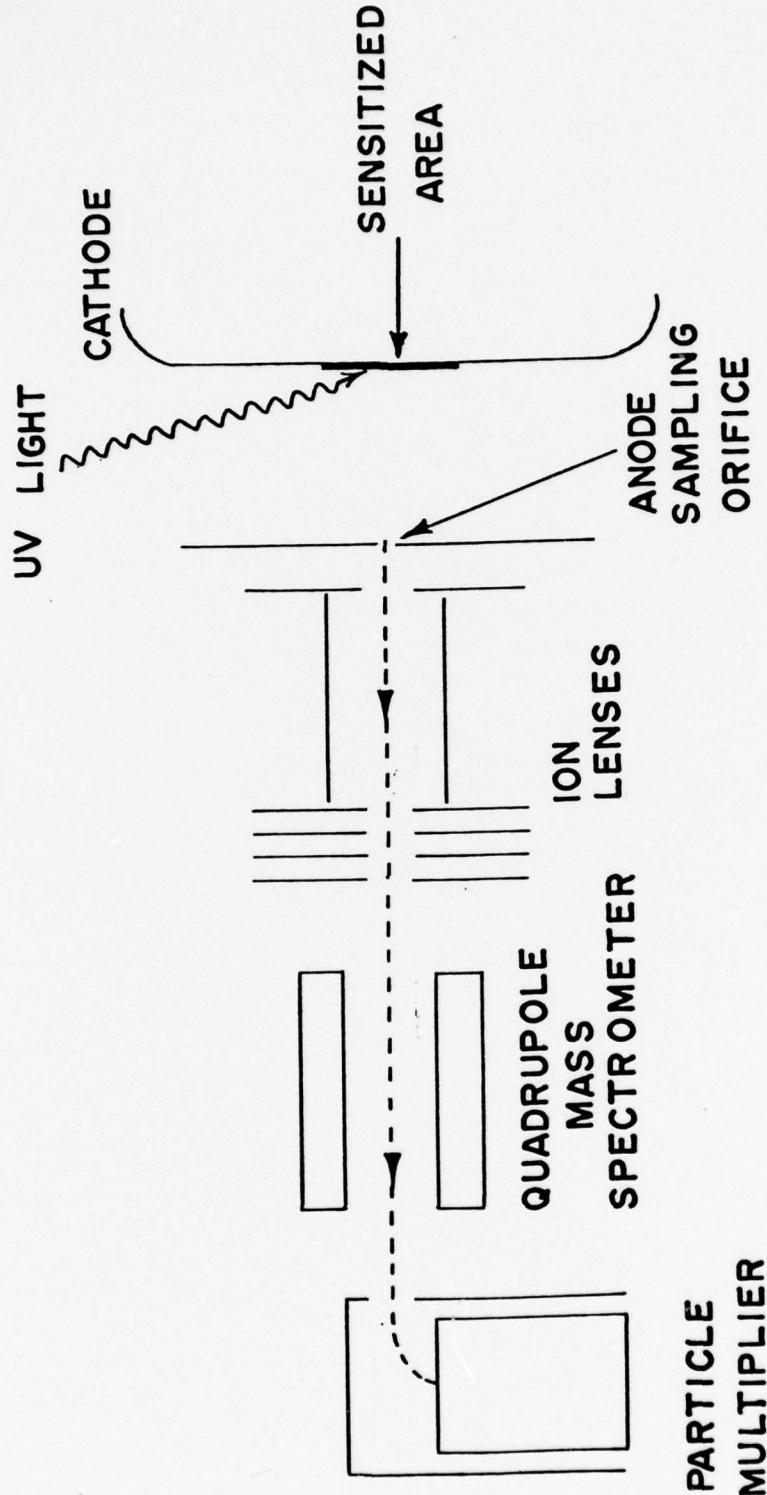
and k is independent of energy. This leads to a maximum value of the rate constant of $2 \times 10^{-9} \text{ cm}^3/\text{sec}$, assuming a value of α for H atoms of $7 \times 10^{-25} \text{ cm}^3$. Fehsenfeld's measurement of $1.0 \pm .2 \times 10^{-9} \text{ cm}^3/\text{sec}$ at 300°K is a factor of two smaller than this maximum value. Herzenberg's analysis leads to an energy of 0.3 eV (or 3600°K) below which the rate should be constant. For the plume model, then, a constant rate of $1 \times 10^{-9} \text{ cm}^3/\text{sec}$ should be appropriate.

3. CLUSTERING IN HCl

In the drift tube experiments on HCl the principle ions at low E/N were not Cl^- , but clustered ions, $\text{Cl}^- \cdot \text{N}(\text{HCl})$, where n is the number of HCl molecules attached. A measurement of the rate for formation of the first cluster ion ($n = 1$) was made using the drift tube apparatus.

A schematic diagram of the apparatus is shown in Fig. 2. Photoelectrons are ejected into the drift region by illuminating a 2 cm^2 sensitized area on the cathode with uv radiation. The photoelectron current in vacuum for a freshly prepared copper iodide coating, or for one sensitized by a glow discharge in hydrogen, approached 10^{-7} A . The emission current dropped upon admission of gas, however, and stabilized at $5 \times 10^{-10} \text{ A}$. A small fraction of the negative ions formed in the 2.6 cm drift space passes through an orifice (diam = 0.34mm) into the mass analysis region.

The negative ions are focussed and accelerated by an arrangement of electrostatic lenses. The lense potentials are set for maximum signal detection and are not changed during the course of a run. The ions selectively transmitted through the quadrupole are then accelerated to an energy of 1 keV as they hit the first dynode of a 20 stage Johnston's Laboratory Multiplier, whose pulse output is amplified and counted by an appropriate scaler.



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FIGURE 2. Drift tube mass spectrometer apparatus. The pressure in the drift region was typically 1 Torr and in the detection region about 10^{-6} Torr. The particle multiplier is offset from the axis to improve on the signal-to-noise ratio.

The relative concentration of HCl to N₂ was 730 ppm \pm 3%. The total gas pressure was measured by a Texas Instruments quartz spiral manometer, and was in the range from 0.2 - 5 Torr. The range of E/N was from 1 - 30 Td.

A typical scan of the ³⁵Cl⁻ and ³⁵Cl⁻ + H³⁵Cl count rates as a function of applied electrode voltage is shown in Figure 3. One striking aspect of Fig. 3 is the presence of cluster ions at very low E/N. This effect is due to formation of Cl⁻ by dissociative attachment from CCl₄, which is introduced into the system as a result of the process used to sensitize the photocathode. The large rate for dissociative attachment of CCl₄ at low energies (maximum at \sim 0.02 eV) and rapid decline of the rate increasing electron energy¹¹ are consistent with the observed anomalous cluster formation at low E/N.

Figure 4 shows the results of taking the ratio of the cluster to primary ion count rates and evaluating n_2 , the attachment coefficient. It is assumed here that both the primary and cluster ions are detected with the same overall probability. (The value of n_2/p expresses the results per unit HCl concentration.) From this data a reaction rate for clustering can be calculated provided a drift velocity for Cl⁻ in N₂ is known. Since no data are available, the drift velocity was calculated from the polarization limit of Langevin mobility theory. Thus, at E/N \sim 12 Td, we calculated $k_2 \sim 1 \times 10^{-25} \text{ cm}^6/\text{sec}$ to within a factor of two.

Several steps have been taken to reduce the experimental uncertainty of the data used in Fig. 4. The vacuum chamber was passivated by several fillings of gas before runs. The overall sensitivity of the multiplier changed with time due to contamination by the HCl, however, short data accumulation times (<1 hr) were used to minimize this problem. Errors which have not been corrected are due to mass discrimination of the sampling and detection system. However, since most discrimination would occur against the higher mass,

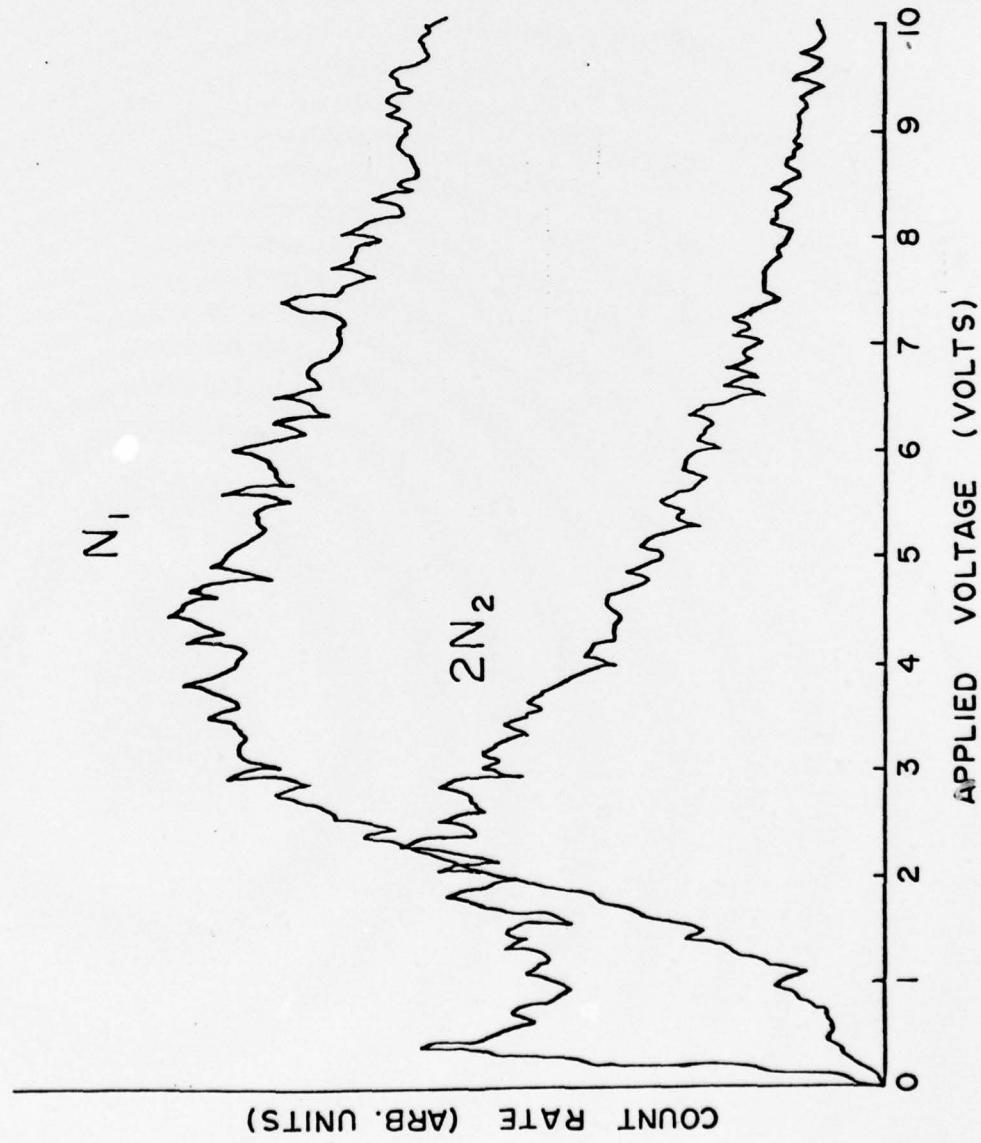


FIGURE 3. Probability for formation of $\text{Cl}^- \cdot \text{HCl}$ ions from Cl^- ions drifting 1 cm in a gas with partial HCl pressure p.

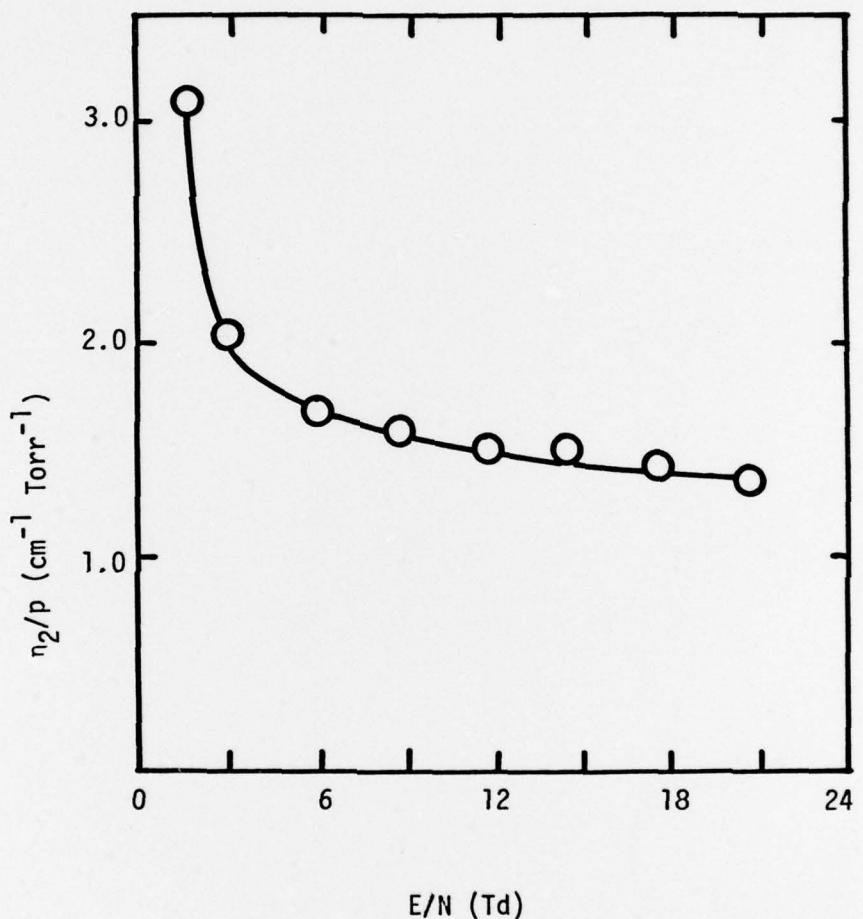


FIGURE 4. Probability for formation of $\text{Cl}^- \cdot \text{HCl}$ ions drifting 1 cm in a gas with partial HCl pressure p .

the reported clustering rate is a lower limit with respect to this systematic error.

An article describing this measurement has been submitted to the Journal of Chemical Physics.

It should be pointed out that 10^{-25} cm⁶/sec is a very large rate constant and implies that at low temperature the clustered ion will dominate. As the temperature rises the collisional destruction of the cluster becomes more likely. Kebarle⁶ has measured the equilibrium rate constant for the process and finds $k_{eq} = 1$ at a pressure of 1 Torr and a temperature of about 600°K. The temperature dependence is fast; at 1200°K the ion ratio is 1000:1 in favor of the C1⁻. However, some consideration should be given to the possibility that cluster ions may be important in the late plume. Such clustered ions could form nucleation sites for droplet growth.

4. COLLISIONAL IONIZATION

The collisional ionization of potassium and chlorine, $K + Cl \rightarrow K^+ + Cl^-$, may be an important reaction in the production of free electrons in the plasma. Once Cl^- is formed, the rapid associative detachment reaction, $Cl^- + H \rightarrow HCl + e$, produces free electrons.

We are attempting to measure the cross section for the reaction using crossed atomic beams in the apparatus shown in Fig. 5. As discussed in earlier reports, the potassium vapor in the oven is forced out of the heated nozzle by a supersonic stream of helium-hydrogen mixture. A beam of fast potassium atoms is formed which is variable in energy according to the nozzle temperature and driven gas mixture ratio.

The potassium beam intersects an atomic chlorine beam formed by thermal dissociation in a resistance heated mullite oven. Potassium ions formed in the intersection region will be extracted by suitable grids and counted by an electron multiplier.

During this grant period a potassium beam source has been developed which readily produces an accelerated beam of potassium with a flux of 2×10^{12} atoms/cm²sec at the collision region. Several hours of operation are possible before reloading of the reservoir is necessary. Potassium consumption is about 0.1 gm per hour. Operation time has been limited to one or two hours by clogging of the skimmer with solid potassium and a mechanical cleaner was found unsatisfactory. A heated skimmer has been built and is presently being installed, which we believe will cure this difficulty.

Considerable difficulty has been encountered with rapid loss of gain by particle multipliers exposed to the hot gas from the chlorine beam source. A stage of differential pumping is being installed to reduce the partial pressure of chlorine in the collision chamber.

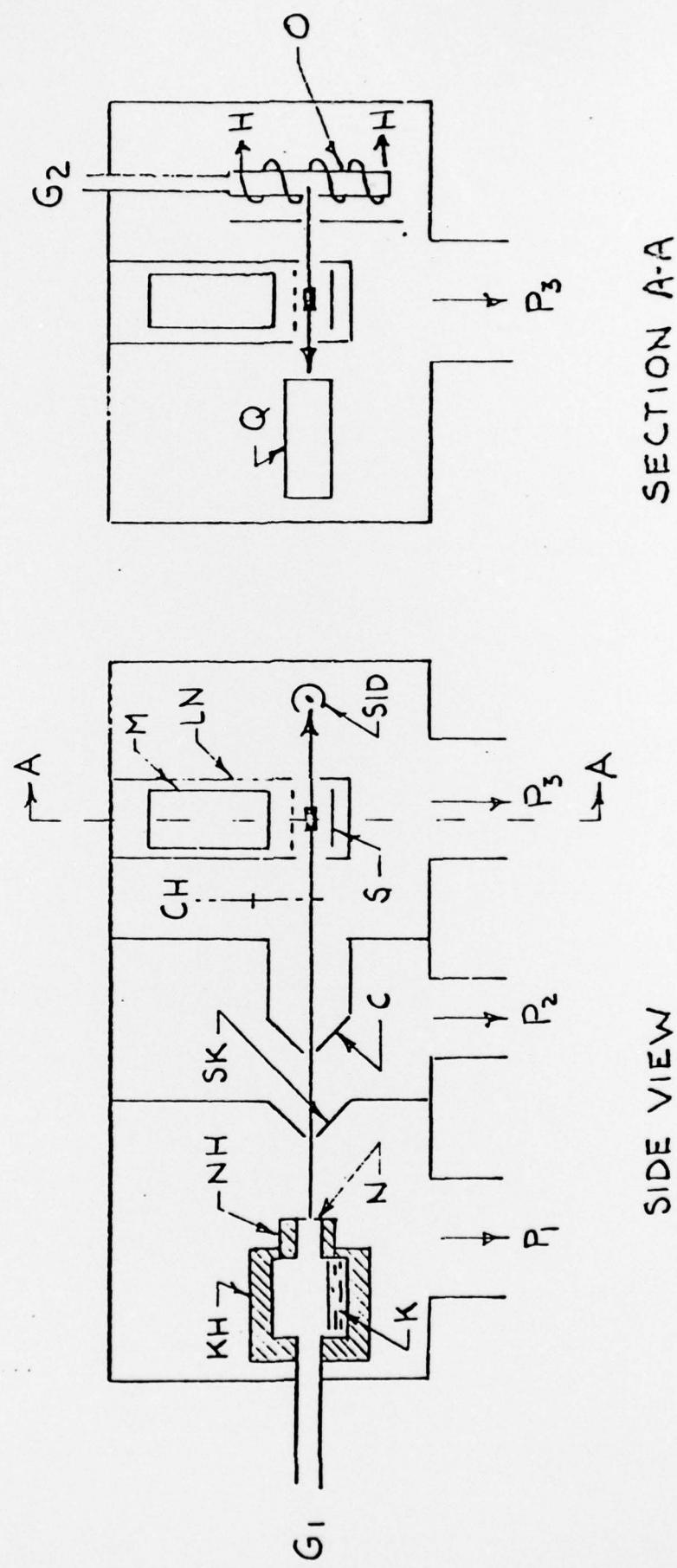


Fig. 5. NOZZLE BEAM APPARATUS. Helium (G_1) flows into potassium oven (KH) which forms reservoir for potassium (K). The nozzle (N) is separately heated (NH). Skimmer (SK) and collimator (CH) form beam which is chopped (C) and monitored by a surface ionization detector (SID). Ions formed at intersection of beams are extracted by sweep plates (S) and counted by cooled (LN) multiplier (M). Section AA shows CH atom oven (O) with heater (H). Fraction of atoms is monitored by mass spectrometer (Q).

The need for an experimental determination of the cross section is evident from the disparate result of three recent theoretical estimates of it. Olsen⁷ has used quantum close coupling techniques to calculate the cross section from threshold to a few eV. The reaction rate derived from this calculation for temperature characteristic of the plume is of the order of three times higher than would be predicted by radar attenuation measurements by Pergament and Jenson.¹ A Landau-Zener curve crossing calculation by Faist and Levine⁸ gives a result about one order of magnitude lower than Olsen. The same treatment gave cross sections in good agreement with experiment for Na-I collisional ionization. A third estimate by Arora⁹ is based on a Born approximation and yields a cross section two orders of magnitude lower than Olsen when extrapolated to threshold energy.

5. THREE-BODY RECOMBINATION IN POTASSIUM

A unique technique has been developed to measure the loss rate of ions and electrons of the alkali metals due to 3-body recombination. The technique involves ionization of the potassium by a pulsed laser, two photon process and analysis of the recombination using the time dependence of a line in the recombination spectrum of the potassium.

The new technique appears to have a number of distinct advantages over the current experimental methods. The measurement of these 3-body rate coefficients is difficult; consequently, despite their importance in controlling ion/electron densities in high pressure plasmas, very few measurements have been made. The most recent work by Sayer et al.¹⁰, for example, is only able to establish an upper limit in the 3-body recombination rate for $\text{Cs}^+ - \text{He} - \text{e}$. Our new technique holds considerable promise in several areas: (a) The optical emission from the radiative recombination process is observed directly. The rate equation for the process are relatively simple and easily solvable; (b) The geometry of the system is very clear. The exciting laser beam establishes a line source of charge in the cell; (c) Since a laser beam of known wavelength and pulse duration is the only excitation mechanism, the kinetic processes in the cell are relatively well-defined.

A partial energy level diagram of potassium is shown in Fig. 6. The method proceeds as follows: Approximately 40 kwatts at 4046 \AA in a 4ns pulse of bandwidth 0.2 \AA excites to saturation the $4^5\text{S}-5^2\text{P}$ transition in a small cell containing K metal vapor at 200°C in a buffer of Argon (0.9 atmospheres). A second 4046 \AA photon ionizes the 5^2P atom. Both processes are saturated; vis: the excitation and photoionization process. Consequently, the initial ion density is a known parameter depending only on the K vapor pressure in the cell.

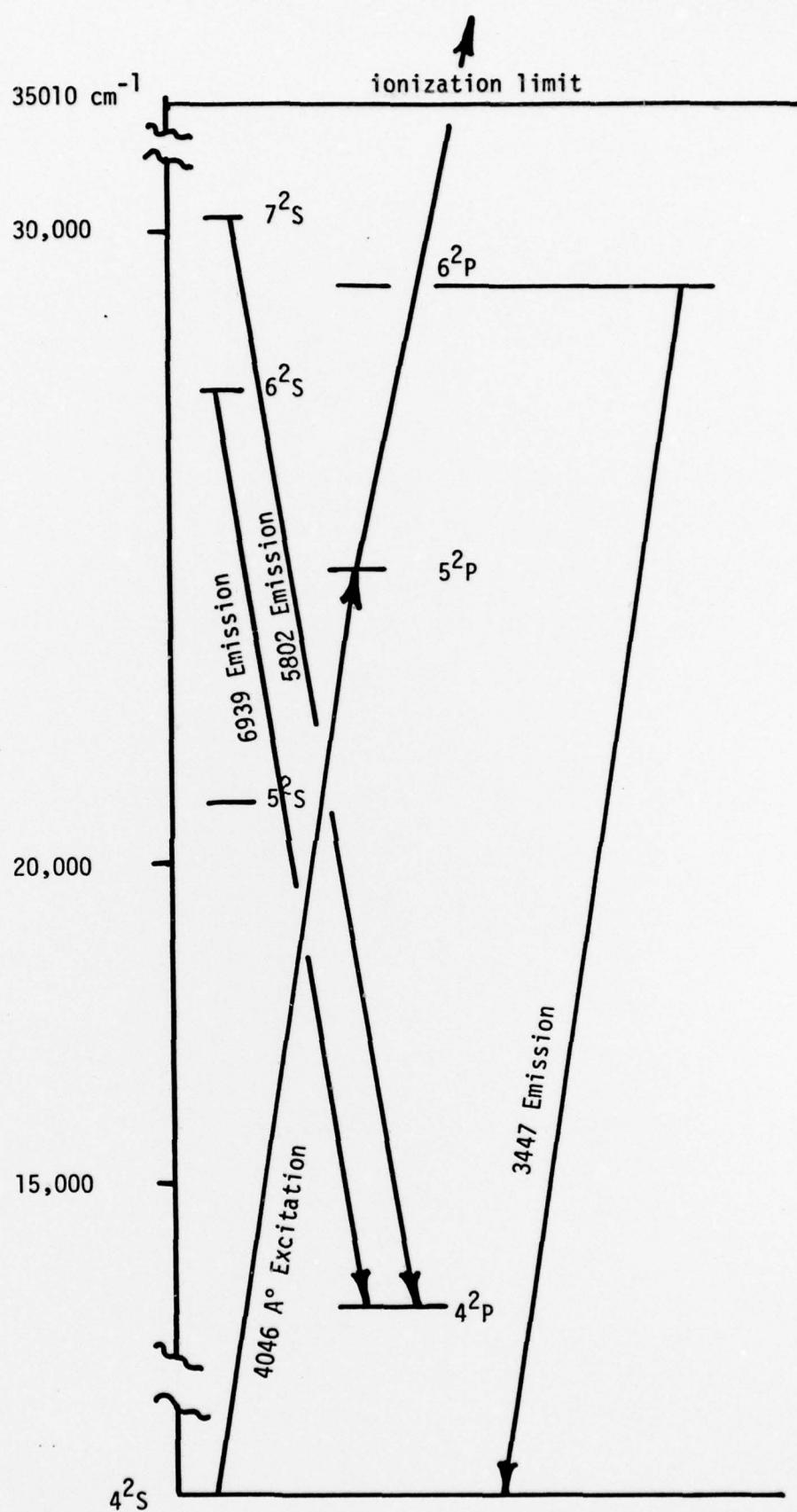


FIGURE 6. Partial energy level diagram for potassium.

The K^+ and electrons recombine in a 3-body process forming an excited atom of K which subsequently decays radiatively. The rate equations are shown below:

$$\frac{dn}{dt} = -\alpha n^2 + (\text{other loss terms such as diffusion})$$

where n is the ion density at the end of the 4ns pulse and K is the recombination rate at a given buffer pressure p (3rd body). And,

$$\frac{dN}{dt} = -\frac{N}{\tau} + \alpha n^2$$

where N is the density of the excited state and τ the radiative decay rate. We find experimentally that the intensity of the emission from the excited state is in the time scale of 200 ns. This time is long compared to radiative decay rates and short compared to ion/electron diffusion times. Consequently, a good approximation to the solution of the coupled rate equations is given by:

$$I(t) = \frac{\alpha N_0^2}{(1 + \alpha N_0 t)^2}$$

where $I(t)$ is the time dependent decay of the emission and N_0 is the initial ion density. A plot of $[I(t)]^{-1/2}$ vs time yields a straight line whose slope is αN_0 .

Emission from the 6^2S-4^2P , 7^2S-4^2P at 6039 Å and 5802 Å respectively are observed. Since the 6^2S and 7^2S levels lie well above the 5^2P level excited by 4046 Å laser beam, these states can only be populated via a 2 photon process, which we have assumed to be a 2 step ionization process followed by radiative recombination to the 6^2S or 7^2S levels.

The 6^2P-4^2S emission can also be observed, however, substantial trapping

of the radiation severely reduces its intensity.

We obtain a preliminary recombination rate constant, $K = 6.3 \times 10^{-28}$ cm⁶/sec for potassium in an argon buffer at 680 Torr and T ≈ 473°K.

A paper on this work has been submitted for presentation at the 30th Annual Meeting of the Gaseous Electronics Conference to be held at Palo Alto, California, October 17 to 19, 1977.

6. TWO-STEP PHOTOIONIZATION OF ALKALI ATOMS.

An experimental measurement of the cross section for photoionization of potassium from the excited 4^2P states was completed earlier in the grant. Publication of the results has been delayed but a paper has now been submitted to the Journal of Chemical Physics. Fig. 7 summarizes the result.

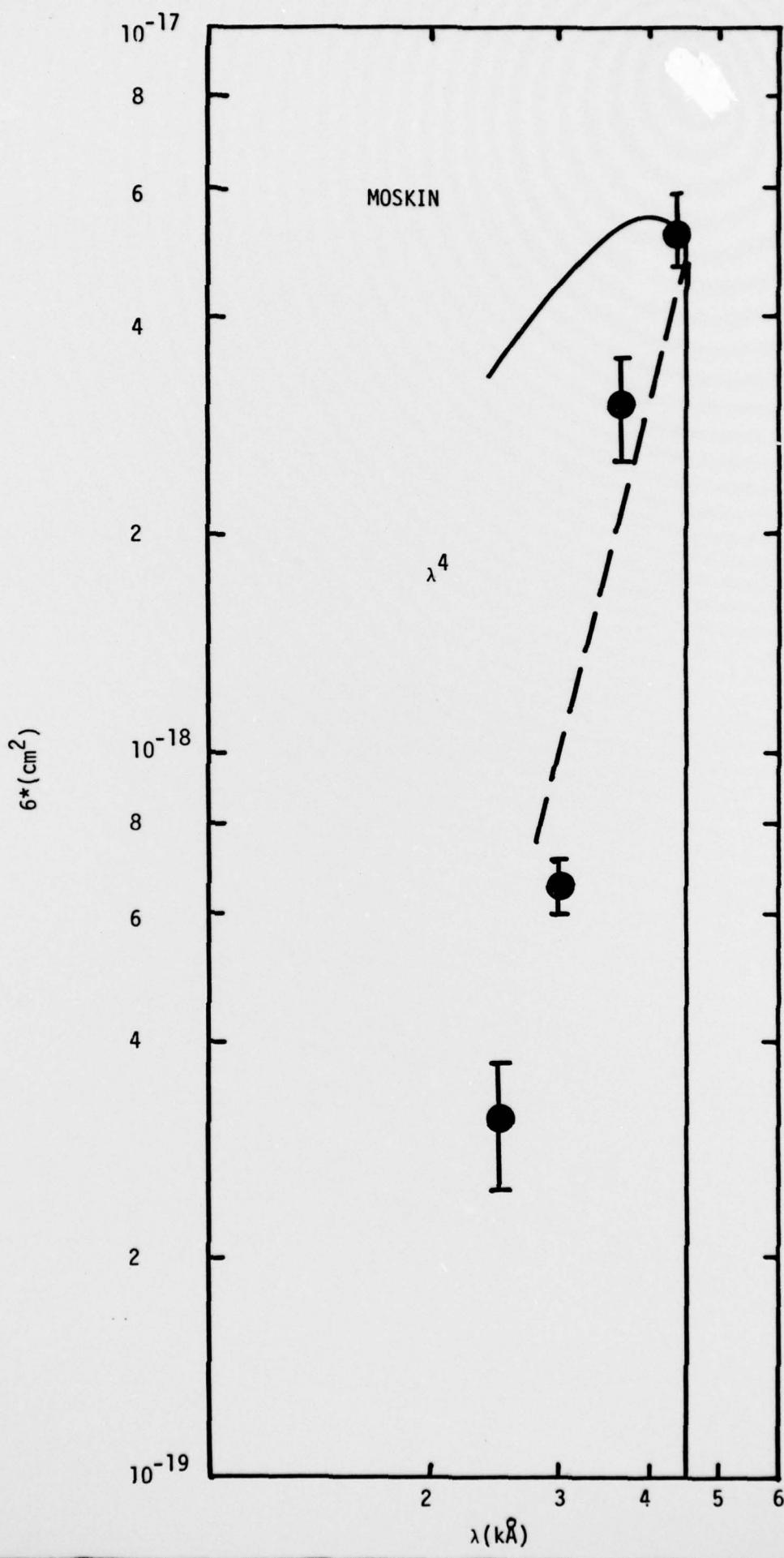


FIGURE 7. Photoionization of excited K atoms.

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| 1. REPORT NUMBER AFOSR/TR-77-1220 | 2. GOVT ACCESSION NO. | 3. CONTRACTOR'S CATALOG NUMBER |
| 4. TITLE (and Subtitle) KINETIC REACTION COEFFICIENTS IN ROCKET EXHAUST PLUMES | 5. TYPE OF REPORT & PERIOD COVERED INTERIM rep. 1 July 1976 - 30 June 1977 | |
| 6. AUTHOR(s) WILLIAM R. SNOW LAIRD D. SCHEARER KAARE J. NYGAARD | 7. CONTRACT OR GRANT NUMBER(s) AFOSR-74-2672 | 8. PROGRAM ELEMENT, PROJECT, TASK & WORK UNIT NUMBERS 2308B2 61102F 17B2 |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS UNIVERSITY OF MISSOURI-ROLLA PHYSICS DEPARTMENT ROLLA, MISSOURI 65401 | 10. REPORT DATE Aug. 77 | 11. NUMBER OF PAGES |
| 11. CONTROLLING OFFICE NAME AND ADDRESS AIRFORCE OFFICE OF SCIENTIFIC RESEARCH/NA BLDG 410 BOLLING AIR FORCE BASE, D.C. 20332 | 12. SECURITY CLASS. (of this report) UNCLASSIFIED | 13. DECLASSIFICATION/DOWNGRADING SCHEDULE |
| 14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (12) 24p. | 15. SECURITY CLASS. (of this report) UNCLASSIFIED | 16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited. |
| 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) (17) DDCI Approved by DDCI | 18. SUPPLEMENTARY NOTES NOV 1 1977 | |
| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) DISSOCIATIVE ATTACHMENT HYDROGEN CHLORDIE ION CLUSTERS COLLISIONAL IONIZATION CHLORINE IONS | 20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A review and analysis of available experiments and theory indicate that the rate constant for associative detachment of H and Cl⁻ is 1x10⁻⁹ cm³/sec and is independent of temperature below 3600°K. The inverse reaction has a threshold energy of 0.64 eV and a preexponential constant of 5 x 10⁻¹⁰ gives a reasonable fit to available measurements. At low temperatures clustering of HCl and Cl⁻ ions is a rapid process. Drift tube measurements yield a value of k=10-25 cm⁶/sec at E/N = 12Td. Progress on a crossed beam measurement of collisional ionization of potassium by atomic chlorine is discussed. A pulsed dye laser has been used to form a K-e plasma in an argon buffer at 680 Torr by a two photon process. Analy- | |

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